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A Mechanism Supported by Extensive Experimental Evidence to Explain High Heat Fluxes Observed During Nucleate Boiling

This paper attempts to elucidate the mechanism responsible for high heat transfer rates occurring in nucleate boiling when liquid films exist on the heating surface. High-speed cinematography and simultaneous transient surface temperature measurements provide a basis for describing the mechanism. In a liquid film, bubbles grow and detach rapidly. The film is quickly renewed. A liquid microlayer exists beneath a bubble its entire life. Conditions are very favorable for rapid evaporation from the microlayer so that heat transfer is rapid. A number of independent observations by other investigators working on diverse problems are cited in support of the mechanism.

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SCOPE

Ebullition sometimes occurs in a thin liquid film on a surface during nucleate boiling. Kusada and Nishikawa (1967) studied nucleate boiling occurring in thin liquid films. They observed that dry out often occurred with water films thinner than 1 mm, and they also generally observed a maximum heat transfer coefficient in this range of thicknesses. Toda and Uchida (1973) have reported achieving exceptionally high heat transfer rates to films of water 0.2 to 0.7 mm thick flowing over a surface at 2 to 10 m/s. Kirby and Westwater (1965) report that such ebullition occurred at high heat fluxes beneath a frothy mixture in their pool boiling studies of methanol and carbon tetrachloride. Katto et al. (1970) report similar observations for water. Numerous studies of boiling in falling liquid films have shown that much higher heat transfer coefficients occur than with pool boiling.

Bubbles growing in a thin liquid film have received little previous study, yet they possibly account for the exceptionally good heat transfer. These bubbles differ markedly from those growing in normal pool boiling in their shorter life and rapid detachment. The significance of these differences has received little consideration.

Ebullition during nucleate boiling generally cools the surface upon which the bubble grows by the evaporation of a thin liquid layer beneath the bubble. This has been

called microlayer evaporation. There has as yet been no report on whether microlayer evaporation occurs during ebullition in thin liquid films.

Bubbles rising through liquid to break at a free surface have been studied by several investigators because they entrain liquid droplets on bursting. Such studies provide a clue to understanding bubbles growing in thin liquid films and how they achieve such rapid departure.

High-speed cinephotography has proven to be a most informative technique for studying bubbles during nucleate boiling. In its use, an unobstructed profile view of the bubble is very helpful, but obtaining such a view is a formidable problem. A serendipitous experiment reported by Williams and Mesler (1967) offered a unique solution. Boiling from an artificial nucleation site produces bubbles so readily from the site that they tend to grow in the thin liquid layer left by a departing bubble.

A useful method of studying microlayer evaporation is to measure the transient surface temperature beneath a growing bubble. A special tiny fast response surface thermocouple has proven useful for this purpose. It must be small enough so that a bubble covers it as the bubble grows.

The relation of transient surface temperature to bubble growth is of vital importance in the investigation. Such information can be obtained by simultaneously photographing with a special high-speed camera the bubble and an oscilloscope screen upon which is displayed the thermocouple signal.

The objective of this study then was to use these tech-

niques to study bubble growth in a thin liquid layer and to determine whether microlayer evaporation occurs. This information is being sought to provide an understanding of the excellent heat transfer through ebullition in thin liquid films during nucleate boiling.

CONCLUSIONS AND SIGNIFICANCE

Bubble life during ebullition in a thin liquid film can be short because of the unique method of detachment that is possible. After the wall of the bubble ruptures, the vapor readily escapes, and the liquid quickly reestablishes a liquid film on the surface.

Microlayer evaporation does occur during ebullition in thin liquid water films. Since bubble life is short, the microlayer does not dry out, at least under the conditions studied. This contrasts with normal pool boiling where dry out is often observed early in the bubble's life, and further microlayer evaporation must wait for the next bubble to grow.

Cooling periods as short as 0.2 ms were observed, and evidence suggests these were caused by small bubbles which were not themselves seen. Longer cooling periods of 0.5, 1.0, and 1.8 ms were definitely related to observed bubbles.

Nucleate boiling, when it occurs in liquid films, offers better heat transfer than otherwise. There are good indications that microlayer vaporization is more effective because of the shorter bubble life in a liquid film and that this is responsible for the improved heat transfer. Further research is necessary to test this hypothesis.

The bubbles which grow in a thin liquid film can be very small and have very short lifetimes. They could easily go unnoticed unless special measures are taken to detect them. The use of the special surface thermocouple adopted for this study is a particularly sensitive means of detection.

For the same total time of microlayer evaporation, several short periods of microlayer evaporation remove more heat than fewer longer periods. The heat transferred varies approximately as the square root of the time of a period but directly with the number of cooling periods. Thus, ebullition in a thin film removes more heat than in normal pool boiling for the same total time of microlayer evaporation.

During forced convection boiling in a tube, nucleate boiling occurs first with liquid filling the tube and then downstream with a liquid film on the wall. An improvement in heat transfer noted downstream from initial nucleate boiling has previously been attributed entirely to convection. Some of this improvement is instead likely due to ebullition in the thin liquid film which develops downstream.

BACKGROUND

Nucleate boiling producing ebullition in thin liquid films appears to offer some unique advantages as a means of transferring heat. This paper reviews pertinent literature and offers new experimental data to analyze this phenomenon.

Toda and Uchida (1973) have studied nucleate boiling occurring in flowing thin liquid films and report higher peak heat fluxes than for normal nucleate boiling. Katto and Kunihiro (1973) report similar results with an impinging liquid jet. Kirby and Westwater (1965) and Katto et al. (1970) report that at high heat fluxes, ebullition occurs in a thin liquid film beneath a frothy mixture of liquid and vapor.

Bubbles are an important element of nucleate boiling and have been studied extensively with the hope of engineering even greater use of the unique advantages of nucleate boiling. Many studies have been concerned with the study of isolated bubbles which grow and depart without interference with other bubbles. Isolated bubbles occur principally at low heat fluxes. At high heat fluxes, there are more bubbles and more opportunity for interference between bubbles. Isolated bubbles are easier to study, but greater use is made of nucleate boiling at the higher heat fluxes.

Although many investigators have noted and reported on bubble interactions, they have received very little consideration in particular. Stock (1960) showed a few frames from a high-speed cinematographic study and commented only that agglomerated bubble sequences were evident in the pictures.

Moissis and Berenson (1963) photographed bubbles at higher heat fluxes and observed continuous vapor columns. To interpret their results, they defined two hydrodynamic transitions in nucleate boiling. The first transition was due to interaction of individual vapor bubbles in a direction perpendicular to the heating surface, and the second was due to lateral interaction of vapor columns.

Zuber (1964) suggested that the heat transfer mechanism changed in going from the region of isolated bubbles to the region of interference and attributed this to a change in the two-phase flow pattern in the vicinity of the heating surface. He further suggested that in the region of isolated bubbles, the heat transfer was by convection, whereas in the region of interference, it was primarily by latent heat transport.

Gaertner (1965) photographed nucleate boiling and concluded that more than one heat transfer mechanism must be involved. He identified four regions that exist in the saturated nucleate pool boiling of liquids from a horizontal surface.

Kirby and Westwater (1965) have photographed nucleate boiling of methanol and carbon tetrachloride from beneath a ground-glass surface. They identified three

general types of distinct bubbles. Type I were isolated bubbles with no interference between bubbles. Type II were bubbles close enough to one another to interfere and coalese. Type III were bubbles growing at high heat fluxes in a thin liquid film beneath a froth of vapor and liquid and were characterized by their ability to suddenly burst, leaving only a small wake as a clue to their disappearance. Kirby (1963) has reported that the heat flux through type III bubbles was especially high and that coalescences took place in less than 200μ sec. Kirby and Westwater (1965) were unique in their observations concerning the rapid detachment possible through bubble coalescence.

Katto et al. (1970) have studied boiling near the peak heat flux with water. They support the Kirby and Westwater (1965) view that at high heat fluxes, ebullition occurs in a liquid film beneath a growing mass of vapor which pushes away surrounding liquid. They propose that it is the loss of this liquid film that is responsible for the peak in the heat flux with increasing surface temperatures.

Iida and Kobayasi (1969) have studied the distribution of vapor above a horizontal surface in pool boiling with a special probe. They found a liquid-rich layer on the surface at high heat fluxes when boiling water. They considered this layer as the region which governs heat transfer.

Nishikawa et al. (1967) studied nucleate boiling with shallow liquid 1 to 30 mm deep covering the surface. They reported that with water, the heat transfer coefficient increased with decreasing depths below 5 mm. Kusada and Nishikawa (1967) extended the study to depths less than 1 mm, where the boiling became unsteady and the surface began to dry. The heat transfer coefficient reached a maximum when water still wet about 70% of the area.

At low liquid levels, Nishikawa et al. (1967) observed that many bubbles coalesced at the free liquid surface to form large surface bubbles similar to soap or froth bubbles. They called them domes. Bubbles larger than 5 mm in diameter were reported for liquid depths less than 5 mm. Beneath these large surface bubbles, a surface cooling was measured of 0.6° to 1.4°C persisting for 20 to 80 ms. A thermocouple at the surface registered these temperatures. The thermocouple was not described as being capable of measuring rapid transients, so actual surface temperature variations may have been greater.

Kusuda and Nishikawa (1967) mentioned that preceding the drying of the entire surface, oscillatory flow of the water film accompanied the growth and collapse of large surface bubbles and that boiling occurred in the water film inside and outside the surface bubbles. They developed a model in which an annular ring film of uniform depth just inside the edge of the bubble evaporated to remove the heat. The calculated thickness of the film was given as 0.034 mm in one case.

Kusuda and Nishikawa (1967) also showed that the large surface bubbles could be partially eliminated by stretching a hot wire above the surface. Elimination of the bubbles reduced the surface temperature improving the heat transfer coefficient.

Nishikawa et al. (1967) have noted that the flow patterns changed as the depth was lowered. Circulation was retarded and bubble population increased at lower liquid levels. They did not speculate on why heat transfer improved with lower liquid levels. They did analyze the behavior of the large surface bubbles and expressed an opinion that the large surface bubbles did not play any important role.

Nucleate boiling in liquid films flowing on vertical surfaces has been the subject of numerous studies. Coulson and Mehta (1953) report that they measured much higher heat transfer coefficients with liquid films of water and

isopropanol than had been reported for pool boiling, particularly at low temperature differences. Rychkov and Pospelov (1959) reported much improved heat transfer coefficients to thin films of aqueous sodium hydroxide solutions as compared to pool boiling. They were able to observe the boiling occurring in the liquid film. Parizhskiy et al. (1972) studied boiling heat transfer to falling films of ammonia. They report that distributing a boiling liquid refrigerant in a film on the surface provides for higher rates of heat transfer than pool boiling. Reduction of film thickness augmented the heat transfer rate. Norman and McIntyre (1960) studied boiling to films of water and reported a decrease in heat transfer coefficient as the liquid flow rate was increased above the minimum wetting rate. They described their coefficients to boiling water films as comparable with those reported for nucleate boiling on a submerged surface. They observed that boiling in the liquid film brought about a marked reduction in the flow rate necessary to maintain a wetted surface.

Fletcher et al. (1974) have studied evaporation of thin water films flowing over horizontal tubes. They observed heat transfer coefficients much higher than had been reported for pool boiling.

Desalination research has demonstrated that the performance of a smooth vertical evaporator tube for thin-film evaporation can be greatly improved through surface modification. Carnavos (1965) described a fluted surface with eighty longitudinal grooves and ridges around the circumference of a 75 mm diameter tube. He reported much higher boiling coefficients with the fluted surface than with a smooth surface. Thomas and Young (1970) clamped longitudinal rectangular fins to the inside surface of a vertical tube. They report that the evaporative heat transfer coefficient of thin films of water flowing down the inside of the tubes was markedly increased by the fins. Thomas and Alexander (1970) have described an improved high performance fluted tube for thin-film evaporation which they report has markedly better performance than a coventional fluted tube.

Although there is agreement that fluted or similarly modified surfaces are better, there is no general understanding of this.

There have been several studies of boiling from artificial nucleation sites. Among these have been Yatabe and Westwater (1966), Howell and Siegel (1966), and Williams and Mesler (1967). All of these studies show that bubbles are more likely to grow from holes or other cavities than from nearby natural sites on the surface. On a horizontal surface, an artificial site is likely to produce bubbles so readily that there is no delay time between bubbles.

Bubbles, when they grow on a surface during nucleate boiling, cool the surface upon which they grow. A microlayer of liquid trapped between the bubble and the surface rapidly evaporates into the bubble producing significant cooling.

Hospeti and Mesler (1969) have studied the surface temperatures beneath water vapor bubbles of various shapes at atmospheric pressure. Their results show that the cooling due to microlayer evaporation persisted for only a fraction of the time a bubble remained on the surface because the microlayer dried out while the bubble was still on the surface. Bubbles remained on the surface for 10 ms or longer, while cooling persisted for only 2 to 6 us.

or longer, while cooling persisted for only 2 to 6 ms.

At higher heat fluxes, bubbles begin to interact, and the effect of this interaction upon microlayer evaporation has not previously been discussed in the literature.

With the isolated bubbles, dry out limits the opportunity for microlayer evaporation. Anything that would shorten bubble life could tend to increase heat transfer by microlayer evaporation.

It has already been observed by Kirby and Westwater (1965) that their type III bubbles which grow in a thin liquid film have a short life and an exceedingly fast detachment. Kirby (1963) also commented upon the high heat transfer rate indicated by such bubble growth.

Growth of a bubble in a thin liquid film is a neglected topic in the literature. An approximation to bubble growth in a thin liquid film is seen when a bubble grows soon after the depature of a larger preceding bubble. An example of such behavior is shown in Figure 1, taken from Williams and Mesler (1967). The way such a bubble detaches from the surface is entirely different from the usual manner. Once the bubble breaks through to the neighboring vapor space, it ruptures the liquid film of the top bubble wall. The vapor in the bubble readily escapes. The liquid film on the surface is rapidly reestablished. The bubble at 10.4 ms in Figure 1 is gone completely, and the solid surface is again covered with a liquid film after only 1.3 ms.

Foam in a boiling liquid film apparently has a beneficial effect on the heat transfer coefficient. Kirschbaum (1952) suggested that an increase in film coefficient arises from the foaming character of the liquid. Coulson and Mehta (1953) report that the addition of a surface active agent has a pronounced effect on the working of the climbing film evaporator that they studied. Sephton (1971) has reported that very small amounts of selected surfactants acting as foaming agents improved the overall heat transfer coefficient in the vertical tube evaporators he studied.

There is a similarity between the bubbles growing quickly in a liquid film and the bubbles which rise through a liquid to a free surface and coalesce with the gas above. This latter case has received considerable study by Newitt et al. (1954) and by Blanchard (1963) among others because in that process, small liquid drops are expelled into the gas. Results of those studies provide useful information for the problem at hand. Some of the drops result from the breakup of the top bubble wall. This wall disappears in just a few microseconds. Other drops are formed from a jet created at the center of the surface depression as the submerged bubble wall converges on the center. Bubbles at the surface actually burst because of internal pressure as shown by Newitt et al. (1954). For small bubbles (0.1 mm), few if any drops results from top bubble wall disappearance according to Day (1964).

The rapid disappearance of the top bubble wall is evident in both cases. A jet cannot form with a bubble bursting from a thin liquid layer because of the absence of underlying liquid. However, the rapid reestablishment of the liquid film in the one case is consistent with the flow leading to jet formation in the other.

Once it is recognized that boiling from a thin liquid film can be important, then a new interpretation of a previous experiment suggests itself. Robinson and Katz (1951) studied the boiling of Freon 12 outside a horizontal copper tube. They reported that injecting vapor beneath the tube improved the rate of heat transfer. Their interpretation was that the injected vapor provided a measure of agitation which improved the heat transfer. An alternate interpretation now would be that the injected vapor flowing past the tube would provide an opportunity for boiling to occur from a thin liquid film. Boiling in the film, as we see, could contribute to the improved heat transfer.

A hysteresis effect has been observed by many investigators. Boiling from a liquid film could be involved. Corty and Foust (1955) observed the hysteresis in boiling *n*-pentane, ether, and Freon 113 from a horizontal surface. Higher temperature differences were measured at first as the heat flux was increased than later when the heat flux was decreased. Their explanation was that nu-

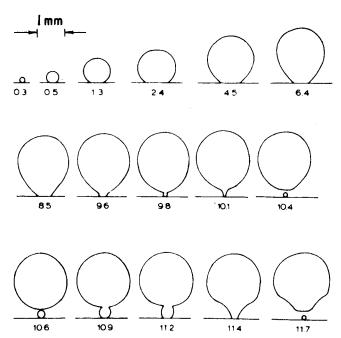


Fig. 1. Bubbles growing at a good artificial nucleation site (from Williams and Mesler, 1967).

cleation centers which had become active at the higher heat fluxes remained active as the heat flux was decreased. At low heat fluxes, there is little doubt that this is the case. At higher heat fluxes, it could also be that as the heat flux was decreased, nucleate boiling persisted in a liquid film. Flow patterns established at higher heat fluxes were observed to persist as the heat flux was lowered.

Pool boiling heat transfer coefficients improve as the heat flux increases. At higher heat fluxes, more ebullition occurs in a liquid film on the surface. Independent experiments show that boiling heat transfer coefficients are better with liquid films than with pool boiling. These facts support a hypothesis that it is the development of ebullition in the liquid film that accounts for the improvement in heat transfer coefficient as the heat flux increases. Further experimental tests of this hypothesis would be interesting.

The purpose of this paper is to report on a bubble growing so soon after a preceding bubble that the bubble was quickly absorbed into the larger preceding bubble. The surface temperature beneath the bubble was measured for evidence of cooling by microlayer evaporation. This situation was considered an approximation to bubble growth in a liquid film which allowed a clear, unobstructed view of the phenomenon.

EXPERIMENTAL WORK

Water at atmospheric pressure was boiled on a surface instrumented with a fast response surface thermocouple of the type used by Moore and Mesler (1961) and described by Kovács and Mesler (1964). Other results on the same apparatus have already been reported by Johnson et al. (1966).

ratus have already been reported by Johnson et al. (1966). The boiling surface was a strip of Chromel P $6 \times 1.6 \times 25$ mm mounted in a metallographer's Bakelite mount. DC current from batteries heated the strip. The thermocouple was a 0.13 mm Alumel wire insulated with a thin aluminum oxide film and rigidly held inside a Chromel P tube, 0.64 mm O.D. This was installed in the Chromel P surface by drawing it through a 0.64 mm hole and then cutting and polishing it flush with the surface. A tiny scratch bridged metal across the aluminum oxide to form the junction. A hole drilled with a 0.04 mm diameter drill near the thermocouple junction functioned as an artificial nucleation site.

A dual lens Fastax WF-17 high-speed motion picture camera was used to photograph simultaneously the bubbles and an oscilloscope face upon which was displayed the thermocouple

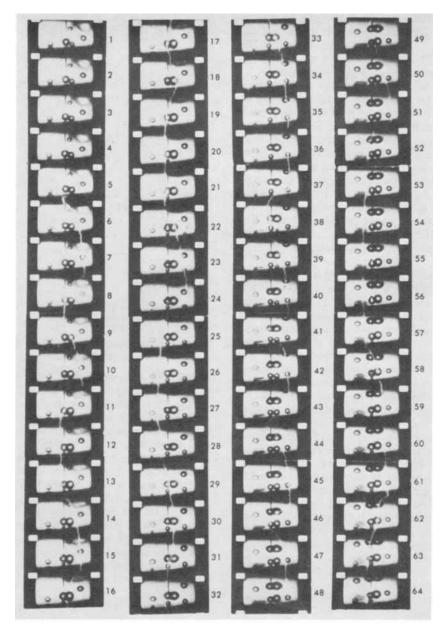


Fig. 2. Bubble growth surface at 2 800 frames/s with superimposed surface temperature shown 5 frames later than the corresponding picture.

signal. The camera recorded the thermocouple signal five frames behind the frame recording the bubble picture. The moving film provided the time base.

The artificial nucleation site was located near the thermocouple junction so that bubbles would have a tendency to grow over the thermocouple and not elsewhere. This arrangement afforded a view of growing bubbles unobstructed by other bubbles. A small wire was hung in the water so that it pointed to the location of the thermocouple. This provided a means of focusing the lens on the bubble location. Extension tubes were used to get a close-up view of the bubbles.

RESULTS

Figure 2 shows 64 successive frames taken at 2 800 frames/s. The white line through the scene indicates the temperature. Lower temperatures are toward the left. The heat flux was 41 000 W/m² [13 000 B.t.u./(hr.) (ft²)] and the average surface temperature 105°C. From one side of a frame to the other is 11 mm and 7°C. This sequence is 1.6 ft of 16 mm film and covers 23 ms. It was chosen as representative of the rest of the 100 ft of film taken at the same time. This film was only one of several taken. It shows coalescence better than the others.

Figure 3 is a tracing made from Figure 2 to show the more important features. In preparing the tracing, the oscilloscope trace was advanced five frames to register it with the bubble images. In the following discussion, all temperatures refers to Figure 3.

A departing bubble is seen in frames 1 and 2. Frames 3 and 4, 6 through 8, and 11 through 16 show tiny bubbles that grow and disappear into the departing bubble. Each of these bubbles cools the surface by about 2°C as seen in frames 3 and 4, 6 through 8, and 11 through 16 for about 0.5, 1.0, and 1.8 ms, respectively.

At frame 19, another bubble 4 starts, and this does not coalesce into the preceding bubble. At frame 45, bubble 4 detaches. A new bubble 5 starts in frame 46 and coalesces into the preceding bubble 4 by frame 54. Still another bubble 6 starts in frame 57.

The cooling from bubble 4 starts in frame 19 and continues to 22 when the temperature starts back up. However, the temperature does not fully recover until frame 32. Interesting cooling periods occur at frames 32 and 33, 36, 38, and 41 for periods of about 0.2 ms each. Although small bubbles cannot be seen, they are the likely cause of

these coolings. Examination of successive frames of the existing bubble shows it to begin shimmering in frame 33 as if set in motion by the capture of a bubble beneath it. Shimmering due to bubble capture occurs earlier and is clearly identified in frames 6, 7, 10, and 11 and in other frames.

Cooling due to bubble 5 is seen from 46 through 52, lasting for 2 ms. Cooling due to bubble 6 begins in frame 57.

ANALYSIS

The amount of heat that must be removed to produce the observed surface cooling can be estimated with a simple model. Assume that the temperatures measured are the temperatures of the surface of a semiinfinite solid and that the temperature suddenly changes from one value to another for a short period. Solving the heat conduction

equation gives $\frac{Q}{A} = \frac{2\Delta T k \sqrt{t}}{\sqrt{\pi \alpha}}$ for the heat flow necessary to cause the cooling.

The three cooling periods in frame 3 through 19 then remove 500, 700, and 900 J/m². This corresponds to a rate of 370 000 W/m² over the 5.7 ms from frame 3 to 19. Heat was supplied at the rate of only 41 000 W/m². During frames 3 through 19, heat was then removed at almost ten times the average supply rate. Of course, only the small area under the tiny bubble was being cooled at this rate, and the period analyzed was only a short while.

The small size of the bubbles growing in the thin liquid film imposes additional considerations on measuring the transient surface temperature beneath bubbles. The contact diameter is at most 0.25 mm in Figure 2. The thermometer must sense the temperature of an area smaller than this if it is expected to measure the full extent of the temperature fluctuations beneath the bubble. Also, since the bubbles are so small, the temperature sensed at any one point will be representative of the surface temperature of a smaller area. If the area close to the thermometer contains a good nucleation site, or is not representative in some other way, then the temperature sensed will not be representative of the rest of the surface.

Some differences can be expected between the situation studied here and the general case of nucleate boiling in a thin liquid film. Higher surface temperatures are necessary for nucleation without an artificial nucleation site. Therefore, larger temperature drops would be likely and microlayer evaporation more rapid. Microlayer dry out would be unlikely in the short contact time, and more heat should be transferred by microlayer evaporation, especially if the bubble frequency were higher.

Forced convection boiling in a tube also affords an opportunity for ebullition from a thin liquid film. Consider the case of a vertical tube with liquid fed into the bottom and vapor issuing from the top. Several complicated flow regimes occur along the tube. Convection without ebullition occurs at the inlet, then subcooled nucleate boiling, and then nucleate boiling. As vapor accumulates in the stream, slug flow develops. Finally, an annular flow develops in which there is a liquid film on the wall and droplets dispersed in the vapor. Hewitt and Hall-Taylor (1970) indicate that annular flow occurs through a large portion of the tube when outlet quality is high. They further indicate that nucleate boiling occurs in the thinning annular liquid film until the film is so thin that good heat transfer through it prevents the attainment of a sufficient wall temperature to allow bubble nucleation at the solid surface. Further nucleation is suppressed. Excellent heat transfer through the annular film in which ebullition occurs has previously been attributed largely to convection

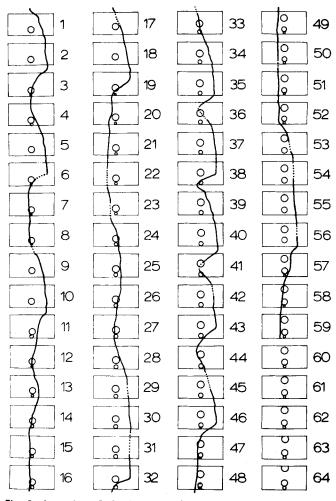


Fig. 3. A tracing of the important features of Figure 2 with the oscilloscope indication advanced 5 frames so that it corresponds with the simultaneous bubble picture.

by Dengler and Addoms (1956), Chen (1966), and others who have attempted to correlate forced convection boiling data. There was no recognition that ebullition in a thin liquid film itself offers excellent heat transfer as has now been reported by so many.

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NOTATION

 $A = \text{area, m}^2$

 $k = \text{thermal conductivity, W/m }^{\circ}K$

Q = heat, Jt = time, s

 ΔT = temperature difference, °K

 α = thermal diffusivity, m²/s

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Surface Reaction with Combined Forced and Free Convection

The influence of combined forced and free convection on the surface reaction of a laminarly flowing species in a rectangular channel is studied. The free convective motion, which is superimposed upon the main axial flow, arises from a transverse density gradient produced by the release of a reaction product, or heat, at the channel wall. A numerical stream function-vorticity method is employed to solve the three-dimensional conservation equations in the case of large Schmidt number. Effects of aspect ratio, diffusivity ratio, surface reaction rate, and Rayleigh number upon the overall reactant conversion rate and local Sherwood number are examined. Reasonable agreement is obtained with experimental data for a hydrochloric acid-calcium carbonate surface reaction.

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